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A STUDY OF THE EFFECT OF VACUUM AND PRESSURE APPLIED TO DIFFERENTIAL THERMAL ANALYSIS

Charles G. Miller, Jr.

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OF
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A STUDY OF THE EFFECT OF VACUUM
AND PRESSURE APPLIED TO DIFFER-
ENTIAL THERMAL ANALYSIS

Charles G. Miller, Jr.

Submitted to the Faculty of
Rensselaer Polytechnic Institute
In Partial Fulfillment of the Requirements
for the Degree of
Master of Civil Engineering

by
Charles G. Miller, Jr.

May 1954

The
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To Professor Edward James Kilcawley, who first aroused the interest of the author in this study; who provided certain background material necessary for an understanding of the nature of the study; who allowed the author complete freedom of investigation, but above all else, the author is most grateful for the encouragement and advice offered throughout the progress of the work.

To Assistant Professor John Emil Munzer, for his patience throughout the indoctrination of the author in the use of the equipment; for his ready assistance in all phases of operation of the equipment; and for his many helpful suggestions and competent technical advice; the author is deeply indebted and most grateful.

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PREFACE

As is indicated by the title of this thesis, the author intended to study the effect of both vacuum and pressure on the process of differential thermal analysis. However, because of unavoidable time delays, in the procurement of the material necessary to convert the existing equipment, there was not sufficient time available for the study of the effect of both vacuum and pressure. Therefore, the scope of this paper has been reduced, and only the study of the effect of a vacuum on the process has been accomplished. This study is recorded in the following pages.

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INTRODUCTION

In working with clays and soils, great difficulty is often encountered in identifying the minerals in the finer fractions. Inasmuch as it is these finer fractions which have great effects on the engineering properties of soils, it is necessary that a satisfactory method of identification be evolved. The petrographic method is satisfactory for the larger grain size range; X-Ray diffraction will show certain crystal characteristics of the finer grains when they occur in fairly large proportions; chemical analysis will give an accurate analysis, but the method is time consuming, expensive, and the results do not indicate the manner in which the constituents are combined.

Differential thermal analysis is a technique for the study of certain thermal characteristics of clay minerals. Basically, differential thermal analysis consists of comparing the thermal properties of an active substance with those of an inactive substance while both materials are being heated at a constant rate. During this heating process, changes occur in the structure and adsorbed moisture content of the soil particles,

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NOTE:
Throughout the paper, all numbers in parenthesis refer to corresponding item numbers in the Bibliography.

and this results in the release or imbibition of heat. Since there are no structural changes in the inert material, the difference in temperature between the soil and the inert material is a measure of the change occurring in the soil. Each mineral has a characteristic curve of thermal change.

Initial investigations of minerals using this method are credited to Le Chatelier (1887), who is generally acknowledged as the originator of the technique. A few years later with Saladin (1904), Le Chatelier presented a paper describing a modified apparatus, but they were unable to get reproducible curves.

In the period that followed, Wallock (1913) studied clays while Wohlen (1913) studied clays, bauxite, and allied materials. Houldsworth and Cobb (1922) and Kurnakov and Urazov (1924), applied thermal analysis to similiar substances.

It was not until recent years with the advent of improved recording and temperature control equipment that investigators could obtain reproducible curves or semi-quantitative information. The modern era with an intensified study of all aspects of the technique began in France by Orcel and Caillere (1933) and in the United States with Insley and Ewell (1935). During this period, many papers were presented on the different aspects of differential thermal analysis, some of the more notable

are: Caillere (1933-1934); Dubois (1936); Kazakov and Andrianov (1936) on methods used in differential analysis; Kumanin and Kalnen (1936) on theory; Menshutkin (1936) on history; Orcel (1935) on laterites; Thilo and Schunemann (1937) on pyrophyllite; Wilcox and Bossard (1936) on self-recording apparatus; and Norton (1939), on an evaluation of the method as applied to clay minerals.

Orcel (1935) presented a paper giving thermal curves for most of the clay minerals and for many natural clays. In this paper Orcel suggested the possibility of quanitative measurement as well as qualitative analysis but no analysis was attempted until 1938 when Norton (18) presented his paper.

In recent years the applications of differential thermal analysis have been numerous and varied. Of particular interest to the soils engineer are the critical studies of many clay minerals in 1942 by Grim and Rowland (7), and basic information on the general application of the method presented in 1945 by Speil, Berkelhammer, Pask, and Davies (21).

Research Project 49 of the American Petroleum Institute, conducted by Kerr, Kulp, and Hamilton (13), has added considerably to the available information by their application of a semi-quantitative method of differential thermal analysis to a study of clay mineral

regions throughout the United States. This is part of a project being carried on by the American Petroleum Institute which has as its ultimate goal "to assemble and completely describe a suite of reference samples which might serve for purposes of comparison in the general field of clay mineralogy."

The differential thermal method of analysis of soil samples has as its purpose the identification of the minerals (clay minerals or other minerals of "clay-size" particles) present in the soil, and a determination of the relative abundance of these minerals. The identification of the minerals present in a sample of soil is accomplished by comparing the differential thermal curve obtained from a trial run with the curves obtained from runs on known materials with all runs conducted under similiar physical conditions. A more detailed discussion of the theory involved is made later in this paper.

Work on the identification of clay minerals by differential thermal analysis was initiated at Renssalaer Polytechnic Institute in 1948 by Costello (2), who used a tube furnace for heating the samples, measured the temperatures with a portable potentiometer, and controlled the heating rate by manually operating a variable transformer. In 1949 Bystrowski (1) added an autographic recorder for recording the sample and differential temperatures. In 1950 Hoskins and Hudson (10) added a poten-

tionmeter pyrometer and conducted investigations to ascertain the effect of variable conditions - heating rate, mineral grain size, etc. - on the differential thermal curves of certain minerals. In 1951 Merritt and White (17) conducted further investigations into the effect of the same and other variable factors - pretreatment of sample, ion saturation, weight of sample, ratio of sample weight to standard weight, etc. - which influence a quantitative analysis of clay minerals.
In 1953 Harper and Kitterman (9) made certain refinements of the apparatus in an attempt to minimize experimental errors and obtained differential thermal curves for stated weights of several of the standard clay minerals. The work of the author of this paper is considered to be a logical and practical extension of the experimental work in the improvement of the method of determination of clay mineral content by the use of differential thermal analysis.

THEORY

General

The theory of differential thermal analysis as outlined by Speil in 1945 and modified by Kerr, Kulp, and Hamilton (13) is included in this study to aid in interpreting the test results which are presented later in this paper. The derivation is not entirely rigorous but it does take into account those factors which normally affect the curves within the limits of experimental error.

Two methods of study may be used in connection with the thermal properties of minerals. Either the static or dynamic method of heating may be applied to a substance causing it to undergo chemical or physical changes. The static method, equilibrium dehydration, uses a static method of heating and is concerned with the determination of the percent loss of weight as a function of temperature. This method has certain inherent difficulties of measurement and it is generally believed that the method of differential thermal analysis offers greater possibilities for the study of clay mineral structure.

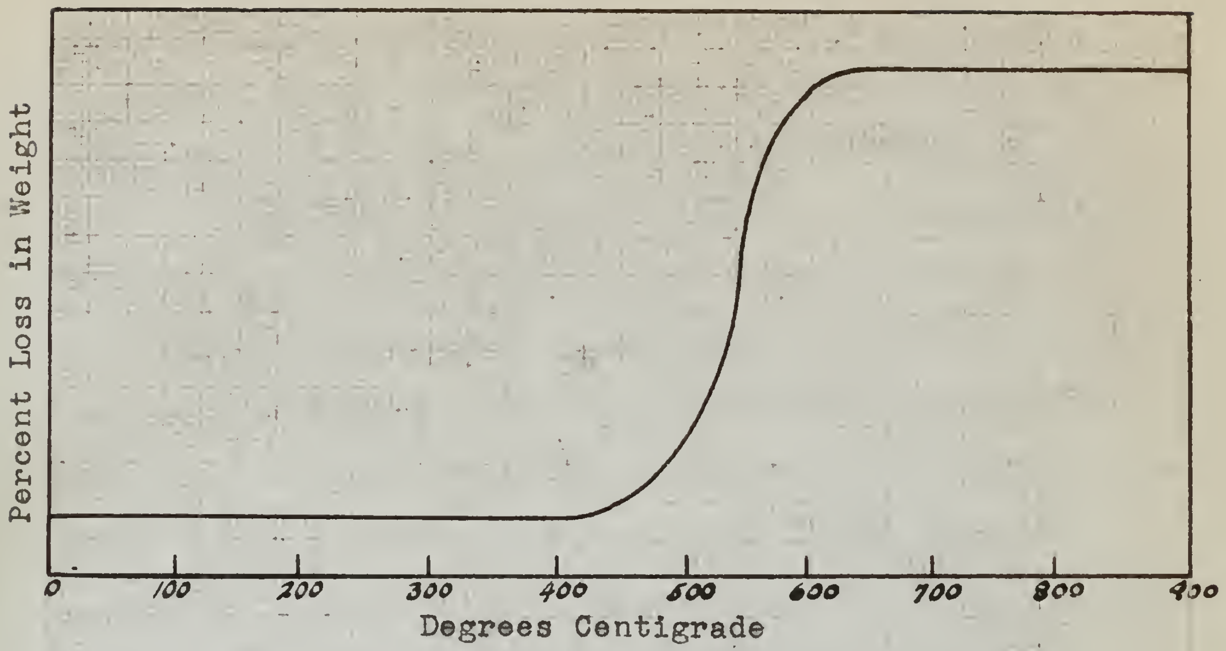
Differential thermal analysis consists of comparing the thermal properties of an active substance with those of a thermally inactive material by heating the materials

at a constant rate up to a temperature of approximately 1100°C.

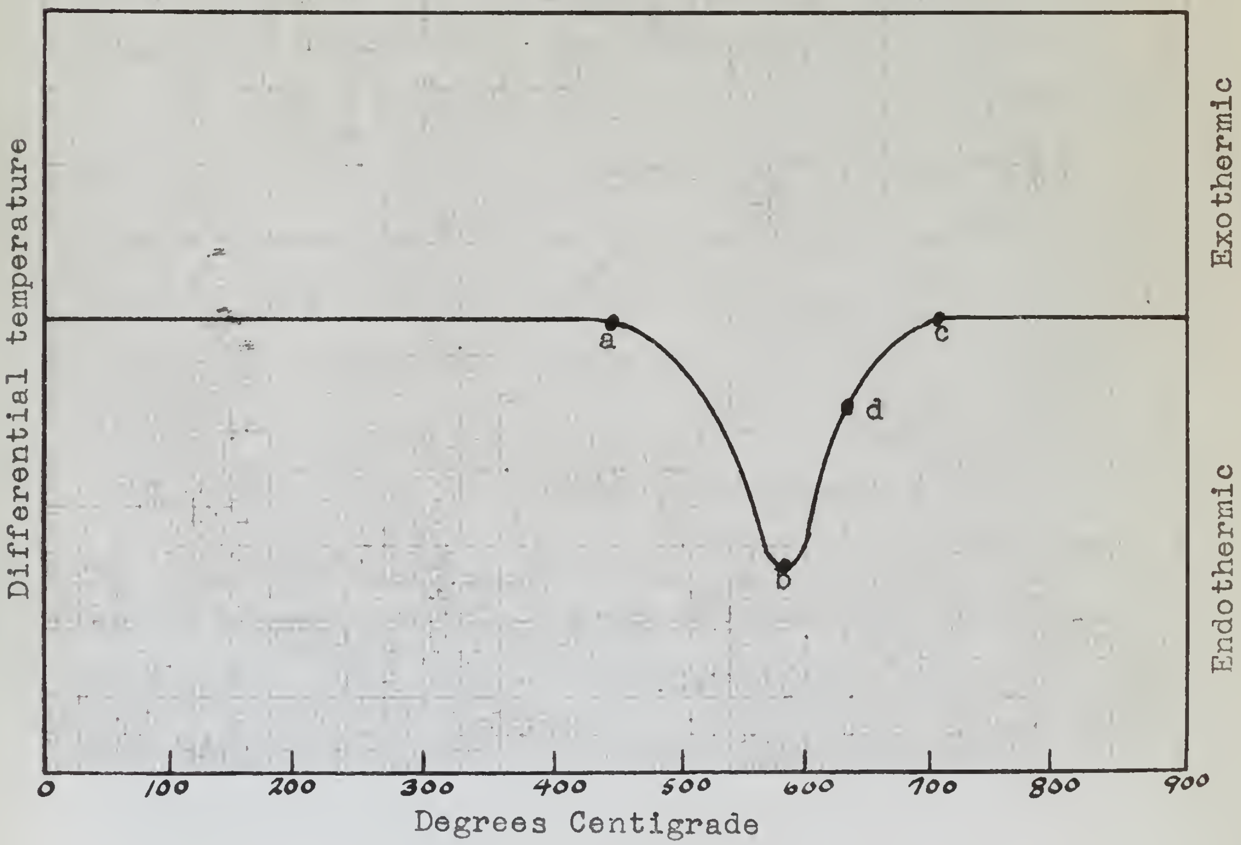
The temperatures of both the active and the inert materials are measured by separate thermocouples, while the difference in temperature between the two materials is measured by a differential thermocouple connecting the two substances. The changes in the active material which cause these differences in temperature may be considered a dehydration process or a decomposition process. Suitable equipment records the temperatures at which the thermal changes take place as well as the intensities of these reactions. The final results appear as a curve showing the temperature difference between the active and inert materials (usually expressed in millivolt equivalents) as a function of the temperature of the active material.

Dehydration produces an endothermic reaction, during which the sample absorbs more heat than the standard, causing the temperature of the sample to lag behind that of the standard. This temperature lag introduces an electrical potential in the differential thermocouple which causes a displacement of the differential temperature curve in a negative direction.

An endothermic reaction peak is shown in Figure 1. Below temperature "a", the heat inflow to both thermocouples, sample and inert material, is the same and no



EQUILIBRIUM DEHYDRATION CURVE



DIFFERENTIAL THERMAL CURVE

FIGURE 1

difference in the temperature is recorded. This straight base line is displaced up or down in small amounts according to the relative thermal conductivity of the specimen and the inert sample, and the specific heats of the specimen and the inert sample. This displacement does not affect the general shape of the curve.

At "a" in Figure 1, the reaction in the mineral proceeds to absorb heat from its surroundings and the sample thermocouple becomes cooler than the thermocouple in the inert material. This effect increases until at "b", the rate of heat absorption by the chemical reaction equals the rate of differential heat conductivity into the specimen. Thereafter, the rate of heat absorption continues to decrease more rapidly than the inflow of heat from the block. At some point "d" between "b" and "c" the reaction ceases. This point is not known, exactly, and therefore points "a" and "c" are usually chosen as the limits of the reaction. Point "c" is the position at which the temperature of both sample and inert material are again identical. The curve "a-b-c" may or may not be symmetrical depending on the nature of the change. If the material has an unusually fine particle size, or if it decreases in mass during decomposition, the back slope may be considerably steeper than the lower temperature slope as a result of competing heat effects.

Decomposition produces an exothermic reaction resulting from a breakdown of the original crystalline structure during which time heat is liberated from the active material causing the temperature of the sample to be higher than that of the standard. The direction of the induced electromotive force in the differential thermocouple due to an exothermic reaction is opposite to that of the flow caused by an endothermic reaction and results in a displacement of the differential temperature curve in a positive direction.

If the sample and standard material are at the same temperature, no electromotive force occurs and the differential thermal curve registers zero millivolts.

Derivation of Equation

The equation developed by Kerr, Kulp, and Hamilton (13), considers the dynamic effects of the differential flow of heat from the sample block to the thermocouples in the center of the sample and the heat absorbed or evolved from the thermal reaction within the sample. This equation was obtained by equating three items:

1. The quantity of heat which flows from the block towards the centers of the two sample cavities and is absorbed by the sample and the standard.
2. The quantity of heat which would be added by an exothermic reaction or subtracted by an endothermic reaction if the sample could be

considered isolated from the block or any other surrounding material.

3. The quantity of heat required in raising the temperature of both the active and inert material.

Inasmuch as the complete derivation is quite lengthy, only the final equation is presented below. In the event the reader desires the complete derivation he is respectfully referred to the paper by Kerr, Kulp, and Hamilton (13), in which this derivation is presented.

Equation: $m = \frac{gk}{\Delta H} \int_c^a \Delta T \, dt$

In which: m = the mass of reactive material in the specimen

g = geometrical shape constant

ΔH = the heat of reaction per unit mass of the reacting material

ΔT = the temperature difference indicated by the differential thermocouple

dt = a differential interval of time

a and c = the integral limits of the differential temperature curve for an endothermic or exothermic reaction.

The above equation neglects the temperature gradient in the sample and the inert material by assuming both gradients are the same. This is based on the assumption that any temperature gradient that may exist is much

smaller than the temperature difference caused by the reaction. The derivation also assumes that the mass of both the test sample and the standard are equal, that temperature differences between the nickle block and the standard are small, and that changes in the mean specific heat and thermal conductivity of the sample are small.

The equation says that the area under the differential curve (as under curve a-b-c in Figure 1) is proportional to the mass of the reacting material. The relationship will be lineal if the thermal conductivity of the materials remains constant throughout the test since the geometrical shape factor and the heat of reaction are constant for a given material and fixed test conditions. However, the work of Kersten (15) has shown that the thermal conductivity of soils does not remain constant but varies with density, moisture content, grading, mineral composition, and mean temperature.

Selecting the limits of the differential temperature curve is purely arbitrary, and for this reason the area under the curve is often difficult to fix. Therefore, many investigators are content with establishing a relationship between the amplitude of the peak reaction and the quantity of the active material contributing to this reaction.

EQUIPMENT

General Description

The equipment used throughout the study was the same basic equipment which has been assembled by previous investigators in the field of Differential Thermal Analysis at Rensselaer Polytechnic Institute. Certain changes in the equipment were necessary to permit the application of a vacuum to the sample holder while the test was being conducted. The equipment has been placed in a different laboratory from that formerly used and this necessitated a few minor changes in the arrangement. A complete description of the basic equipment used and the changes made is given below.

Furnaces

The three electric test furnaces used were horizontal, heavy duty, combustion type, Hoskins Model FH-305, 12 inches long with an inside diameter of 2 1/32 inches. These furnaces all used 1750-watt heating elements supplied by a two-kilowatt transformer with a maximum output of 17 volts and 118 amperes. A switch panel using knife switches was used so as to be able to utilize all of the furnaces with the one transformer. The furnaces normally use a 12-inch combustion tube with an inside diameter of 1 1/2 inches. This tube is made of cemented alumina, is very porous, and is unsuitable for a vacuum process.

Furnace No. 1 was unchanged. In Furnace No. 2, the cemented alumina combustion tube was replaced by a 12-inch combustion tube made of fused quartz and fused silica with a sand surface finish. In Furnace No. 3, the cemented alumina combustion tube was replaced by a 24-inch combustion tube made of fused quartz and fused silica with a sand surface finish. The 24-inch tube was ordered with one end closed and the inside of the other end finely finished for rubber stoppers. These fused silica and fused quartz combustion tubes were procured from the Thermal Syndicate, Ltd, of Lynbrook, New York, under the trademark "Vitreosil."

Sample Holders

The sample holders used in the study were of a type developed by J. E. Munzer of the Faculty of Rensselaer Polytechnic Institute. The sample holder is a machined nickle block with two sample wells, one for the test sample and the other for the thermal standard. The two wells are separated by a slot, 1/16 inch wide and 1/2 inch deep, to reduce the heat transfer between the adjacent wells. Each well is so constructed as to be able to accommodate two thermocouples; one a conventional temperature measuring thermocouple, and the other a differential temperature thermocouple which is used to connect the two wells. The sample holder is secured to a steel rod to facilitate handling. This rod also serves as a convenient stiffener

for the porcelain tube insulators which carry the thermocouple leads inside the furnace.

Thermocouples

All thermocouples were made from Brown and Sharp 18 gage chromel and alumel wire stock and were fused by using an electric arc. This type of thermocouple is very satisfactory because of the small bead at the joint. The differential temperature thermocouple is made of two leads of chromel wire bridged by a short length of alumel wire. The thermocouple junctions are centered in their respective wells in the sample holder and held in place by porcelain tube insulators which carry the thermocouple leads outside of the furnace. There, the leads are connected by means of an octagonal plug to a circuit, which is connected to a terminal block in the cabinet, housing the recording equipment. The use of this second circuit with the octagonal plugs permits easy connection of the recording equipment to any of the sample holders in any of the furnaces.

Thermocouple Tester

A small thermocouple tester developed by Harper and Kitterman (9) was used quite successfully in testing the continuity of the circuits in each sample holder. This tester consists of a small D. C. Ammeter, which, when using a current from a flashlight battery can be connected in succession through a multiple position switch to each of the three thermocouples in the sample holder.

Recording Equipment

A Speedomax - Type G, Model S-60000 Series, self-balancing recording potentiometer, manufactured by Leeds and Northrup Company, is used to record the internal temperature of the sample and the difference between the temperature of the sample and the inert standard as measured by the differential temperature thermocouple. This recorder is capable of recording temperatures from 0 to 1200 degrees centigrade and differential temperatures ranging between plus 1.5 and minus 1.5 millivolt equivalents. When operated as a two-point recorder, the thermal curve is plotted directly on paper calibrated in degrees centigrade with successive points being plotted every six seconds. The evaluation of the differential thermal curve requires the superimposition of an equivalent millivolt scale.

A Brown Recording Potentiometer Pyrometer, Model No. 113661-X53#1-H, manufactured by the Brown Instrument Company is used to record the temperature of the standard and to control the rate of increase in furnace temperature. The thermal standard temperature is printed continuously with a temperature range of 0 to 1200 degrees centigrade.

Temperature Control

Temperature Control is effected by means of a ratio of gears in the chain drive mechanism of the Brown Potentiometer which controls the rate of travel of a pointer across the temperature scale. The actual change in voltage

to the transformer is effected by a motor driven variable transformer, Variac V-20, having a rated output of 3.45 kilowatts and operating between 0 and 135 volts. This Variac is placed in series between the power source and the furnace transformer and therefore it controls the voltage input to the furnace. The Variac is actuated by the relative position of the temperature indicator with respect to the constant travel pointer.

Vacuum Equipment

The vacuum was created by a CENCO Pressurvac 4, pressure-vacuum pump manufactured by the Central Scientific Company. A "U" tube was used as a vacuum gage. This tube was filled with mercury, closed at one end, and connected with a "tee" into the system.

Preparation Apparatus

Materials to be tested were preheated in an Elconap Oven, Model DPC-M-60292, manufactured by the Electric Heat Control Apparatus Co., Newark, New Jersey. A Hevi-Duty Multiple Unit Electric Muffle Furnace, Type 66-P manufactured by the Hevi-Duty Electric Company, Milwaukee, Wisconsin, was available for calibration and checking of thermocouples.

EQUIPMENT CALIBRATION

Recording Equipment

Both autographic recorders are equipped with compensators which automatically correct the millivolt equivalent inputs from the temperature measuring thermocouples for variations in machine cold junction temperatures. The recorders were carefully calibrated during their initial installation by J. E. Munzer and by Hudson and Hoskins. No troubles were encountered in the use of these recorders.

Differential Thermocouples

The differential thermocouples were calibrated to insure their proper reading. This was accomplished by running a differential thermal test with each differential thermocouple in a sample holder and the wells of the sample holder were filled with an equal quantity of inert material, alumina.

Temperature Thermocouples

All thermocouples were calibrated by placing them in the Muffle Furnace with a standard thermocouple and heating them to a temperature of 1000 degrees centigrade. The thermocouples used were those made by Harper and Kitterman (9), who used an electric arc for fusing the ends of the wire together. The two thermocouple wires were used as one electrode and a shallow layer of

mercury submerged in a quenching oil, as the other electrode. This type of welding of the thermocouples produced very satisfactory small beads at the joint.

PROCEDURE

General

The differential thermal procedure is one in which it is of the utmost importance to maintain uniform test conditions in order that reproducible curves can be obtained. This fact, together with the observations made under the theory, permit the listing of certain theoretical requirements which must be taken into consideration in the application of differential thermal analysis. The most important of these requirements, as listed by Lambe (16), are as follows:

1. The mass, specific heat, and thermal conductivity of the sample must be equal to the mass, specific heat, and thermal conductivity of the inert material.
2. The beads of the thermocouples must be located at the centers of the sample and the inert material in their respective cells in the sample holder.
3. The inert material must not have any thermal reaction in the temperature range used (must be truly inert).
4. The mass of the sample holder must be very large with respect to the mass of the sample and the inert material, so that the effect of

an infinite thermal reservoir is created.

5. The sample holder must be symmetrical with respect to the location of the sample cell and the inert material cell.
6. The particle size should be small so as to obtain as great specific surface as practicable.

It was determined by the investigator that the procedures as recommended by Merritt and White (17), which had been developed for use with the equipment assembled at Rensselaer Polytechnic Institute, could be followed in the current investigations, and the investigator would be within the general precepts as outlined by Lambe above.

Clay Mineral Samples

The four clay minerals used in the tests were; H-4 Kaolinite, Macon, Georgia; H-12 Halloysite, Bedford, Indiana; H-24 Bentonite, Otay, California; and H-36 Illite, Morris, Illinois. The clay minerals were obtained from Wards' Natural Science Establishment, Inc. The clays were collected and identified by the American Petroleum Institute Project No. 49 in co-operation with university, industrial, and other laboratories.

The clay samples were ground and sieved. All of the samples used in the investigations were composed of the finer fraction, 200 mesh to pan, grain size. This size was used to obtain as large a specific surface

as practicable.

The sieved material was placed in evaporating dishes in a drying oven set at 40°C for a period of at least 24 hours prior to testing. Because material of this grain size has a tendency to aggregate upon drying, each sample was resieved immediately before being placed in the sample block.

Inert Standard

The standard material used was gamma-aluminum oxide (alumina) from the Aluminum Company of America, Chemicals Division, Pittsburg, Pennsylvania. The material was ground and sieved to the same grain size as the clay minerals, 200 mesh to pan.

Lambe (16) has stated that the alumina picks up moisture very readily from the atmosphere and for this reason must be preheated to at least 250°C, and then cooled, within a few hours previous to each test run. However, certain tests conducted by Harper and Kitterman (9) showed no detrimental effects if the alumina was heated to 300°C and then placed in the 40°C drying oven to remain until placed in sample holder. Accordingly, this was the method used for maintaining the alumina in the same condition for all of the tests conducted.

Heating Rate

The heating rates recommended by many investigators in the field vary from 10° to 15°C per minute

(600° to 900°C per hour) with a major portion of the work being done at 12.5°C per minute (750°C per hour). However, Merritt and White (17) have determined that a heating rate of 17°C per minute (1023°C per hour) for the 1750 watt furnaces is the best heating rate to be used with the equipment on hand. Accordingly, this heating rate of 1023°C per hour was used in all of the tests conducted.

Thermocouples

Prior to placing the sample and standard in their individual cells in the sample holder, the thermocouples were checked to insure that they were not in direct contact with the sample block and that each bead was centered in its cell. Then the porcelin insulators around the thermocouple wires were adjusted so that they were flush with the wall of the cell.

Weights of Sample

All of the samples used in the test runs were of known weight, with the exception of the first few test runs which were made using cell volumes of material. Both the sample and the inert material were weighed to the nearest 0.001 gram on an analytical balance just before being placed in the sample holder. It was decided to use a weight of 0.700 grams of material in all of the tests. For the size of the cells in the sample holders used, this permitted all of the material

to be placed in the cell and still provided a good cover over the thermocouple beads.

Preparation of Sample Holder

When both the sample and the inert material were placed in the holder, extreme care was taken that the thermocouple beads remained in the center of each cell. The material was compacted by tapping the bottom of the cell. This resulted in fairly uniform density and good consolidation without danger of damage to the thermocouple beads. The last step before placing the sample holder in the furnace was a check of the continuity of all of the thermocouple circuits by use of the thermocouple tester assembled by Harper and Kitterman (9).

Operation of Equipment

After the sample holder had been prepared it was placed in the furnace which was to be utilized for the particular run. Then the octagonal plug on the ends of the thermocouples was connected into the circuit with the recording equipment. The batteries for operating the internal circuits of the Brown Potentiometer and the Speedomax were then connected (these batteries were not disconnected between a series of runs but were disconnected only when the equipment was not going to be used for some period of time). The switches to the furnace to be used and to the main power supply were then closed. The electronic circuit of the Speedomax

was allowed to balance, and the electronic circuit of the Brown Potentiometer was balanced manually.

It had been determined by Merritt and White (17), and Harper and Kitterman (9), that a more uniform heating rate and therfore more consistent results could be obtained by turning off the Brown Potentiometer (which controls the travel of the time regulating pointer) after balancing the internal circuit and setting both indicators at 75°C. By properly setting the compensating rheostat, the correct initial voltage from the Variac to the furnace could be established. When the Speedomax indicated a temperature of 75°C had been reached the Brown Potentiometer was turned on and the test was allowed to continue. It has been found that this procedure virtually eliminates the "hunting effect" of the temperature control mechanism. The temperature control indicator, if allowed to continue, will open a mechanical cut-off switch at 1200°C. The cut-off switch activates a relay which automatically shuts off all power to the equipment and furnaces. In the event a cooling curve is desired, the Brown Potentiometer is turned off at 1023°C; the switch to the furnace is opened; and then the Speedomax will continue to operate and will record a cooling curve.

When Vacuum Was Used

For the test runs in which a vacuum was to be applied to the sample, the following procedure was

adopted. The special sample holder with extended porcelin insulators was used. These extended porcelin insulators were required because of the longer combustion tube used. This sample holder had the thermocouple leads going through a rubber stopper. Care must be taken in seating the rubber stopper so as to get a tight fit. A glass tube was extended through the rubber stopper. This glass tube was then connected to the vacuum pump. As mentioned in the section under "Equipment", a glass "U" tube was used as a vacuum gage. After the furnace switch was closed the vacuum pump was started, and the air evacuated to a vacuum of approximately 1 mm of mercury. The system was tight enough to maintain this vacuum for quite a few minutes, but to keep the vacuum constant, the pump operation was continued throughout the experiment.

Data Recorded

In addition to the graphic records which are made automatically by the two recorders, it is considered that the below listed data is essential for proper future use of, or work with, the curves. Therefore, the following data was recorded for each test conducted:

1. Number of the run: This number was marked on each of the curves.
2. Date of the test:
3. Sample tested: The mineral name if known,

and the location from whence it came, if name unknown.

4. Standard used:
5. Grain size of sample and standard:
6. Quantity of sample and standard: By either cell volume or weight in grains.
7. Thermocouple numbers: Each thermocouple was numbered so as to be able to make any corrections necessary because of variations in original calibration.
8. Cold junction temperature: To be able to make the necessary corrections for cold junction variations.
9. The heating rate:
10. The furnace used: This was necessary in the tests the author conducted because each furnace was different (see Equipment section).
11. Remarks: Deviations from standard procedure, equipment, material, or any other pertinent information.

Furnace Cooling

After completion of a test run, six hours or more are required for the furnace to cool to room temperature. This cooling requirement greatly restricts the number of tests which can be completed in a normal work day. Various methods of increasing the cooling rate of the furnaces were tried but without much success. It is

considered that rapid cooling might decrease the life of the heating elements in the furnaces. Therefore maximum utilization of the recording equipment requires at least one additional furnace.

INVESTIGATIONS AND OBSERVATIONS

General

The tests conducted by the author were along three general lines: (a) the first series of tests were conducted to verify the accuracy of the equipment in its present location and to enable the author to become proficient in the use of the equipment; (b) the second series of tests were conducted to study the effects of a change in types of combustion tubes; and the third series of tests were conducted to study the effects of the application of a vacuum to the sample during the thermal analysis.

During the process of evaluating the tests conducted during these investigations, certain fundamental properties of the differential temperature curve became apparent. Some of these properties are discussed at this point to assist in the explanation of the observations which follow.

As was noted in the section "Theory", the temperatures at which the peak endothermic and exothermic reactions take place are a particular property of each clay mineral, and it is this property which makes possible the identification of clay minerals by the process of differential thermal analysis.

The theoretical discussion also indicated that the

areas under the differential temperature curves (therefore, the magnitudes of the peak reactions) are proportional to the mass of the reacting material. It is this fact that makes possible the quantitative analysis of clay minerals.

All of the samples to be tested were dried in an oven at 40°C for at least 24 hours prior to testing. The samples, once dried, stayed in the oven until all of the tests were concluded on that particular type of clay. Repeated tests on these samples over an extended period of time indicated a gradual decrease in the magnitudes of all reactions. It was thus concluded that leaving the samples in the drying oven for more than 24 hours removes not only the hygroscopic moisture but some of the OH lattice water as well.

Clay Mineral Structure

The general thermal characteristics of the four clay minerals used in this investigation are discussed as follows:

H-4 Kaolinite, Macon, Georgia: The thermal curves (see Figure 2) show no evidence of significant impurity. They consist simply of a broad symmetrical endothermic peak at approximately 590°C and a very sharp strong exothermic peak at approximately 990°C. Most investigators agree that the endothermic reaction accompanies the dehydration of the mineral and the exothermic reaction is associated

with the formation of gamma-aluminum oxide. There are a number of investigators, Grim (5), who believe that the loss of OH lattice water is accompanied by a fairly complete loss of structure, and they attribute the oxothermic reaction at 990°C to the formation of mullite.

H-12b Halloysite, Bedford, Indiana: The thermal curves (see Figure #3) show an endothermic peak at approximately 140°C, a second endothermic peak at approximately 575°C, and an exothermic peak at approximately 1000°C. The first endothermic peak is attributed to the loss of water occurring between basal plane surfaces of adjacent unit layers. The second endothermic reaction, due to loss of OH water, tends to develop a peak at a slightly lower temperature than that in the case of kaolinite, but this peak for halloysite is asymmetrical. It is usually more abrupt on the high-temperature side than the similiar peak for kaolinite. The exothermic reaction which occurs is attributed to the formation of gamma-aluminum oxide with the possibility also existing of the formation of some mullite.

H-24 Bentonite, Otay, California: The thermal curve (see Figure 4) shows endothermic peaks at approximately 180°C, 640°C, and 850°C. An exothermic

reaction follows the last endothermic peak and has a peak value at approximately 1020°C. The first endothermic reaction peak indicates the loss of swelling water (that is water held between the basal planes of the lattice structure). The second endothermic peak is attributed to the loss of most of the lattice water. However, the structure is not lost until the third endothermic peak, at which time the last OH water is lost. The exothermic reaction is attributed to the formation of spinel.

H-36 Illite, Morris, Illinois: The thermal curves (see Figure 5) shows endothermic peaks at approximately 140°C, 550°C, and 950°C. As in the case of the bentonite, the first endothermic reaction peak indicates the loss of swelling water. The second endothermic peak is attributed to the loss of most of the lattice water. The third endothermic reaction is characteristic of the loss of the last OH water. This particular illite is a raw clay and it contains a large amount of siderite. This oxidizable material causes a sharp exothermic reaction at approximately 650°C. There is a small exothermic reaction following the third endothermic reaction. This reaction is attributed to the formation of spinel.

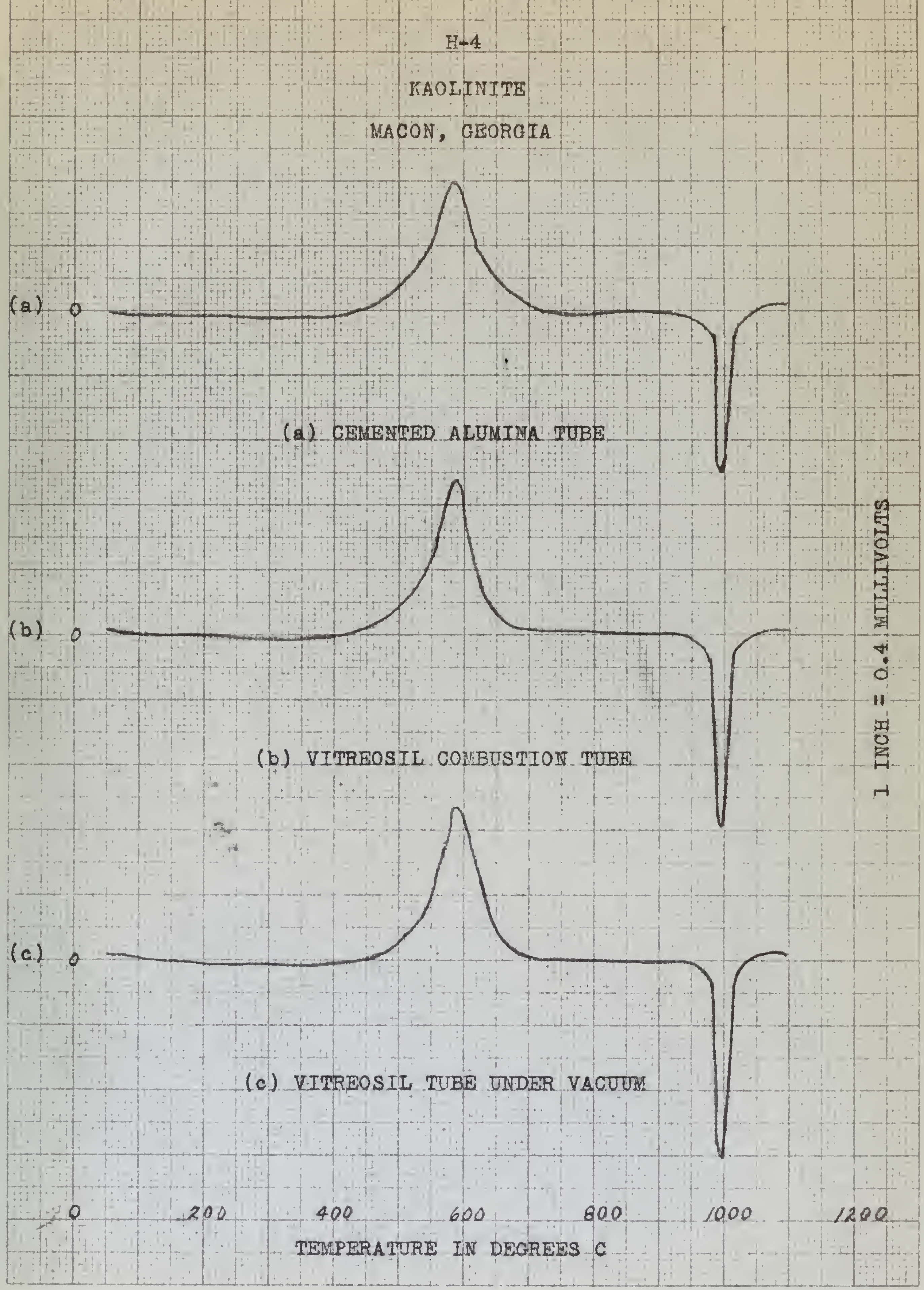

H-4
KAOLINITE
MACON, GEORGIA
(a)
0
(a) CEMENTED ALUMINA TUBE
(b)
0
(b) VITREOSIL COMBUSTION TUBE
(c)
0
(c) VITREOSIL TUBE UNDER VACUUM
1 INCH = 0.4 MILLIVOLTS
0
200
400
600
800
1000
1200
TEMPERATURE IN DEGREES C

FIGURE 2

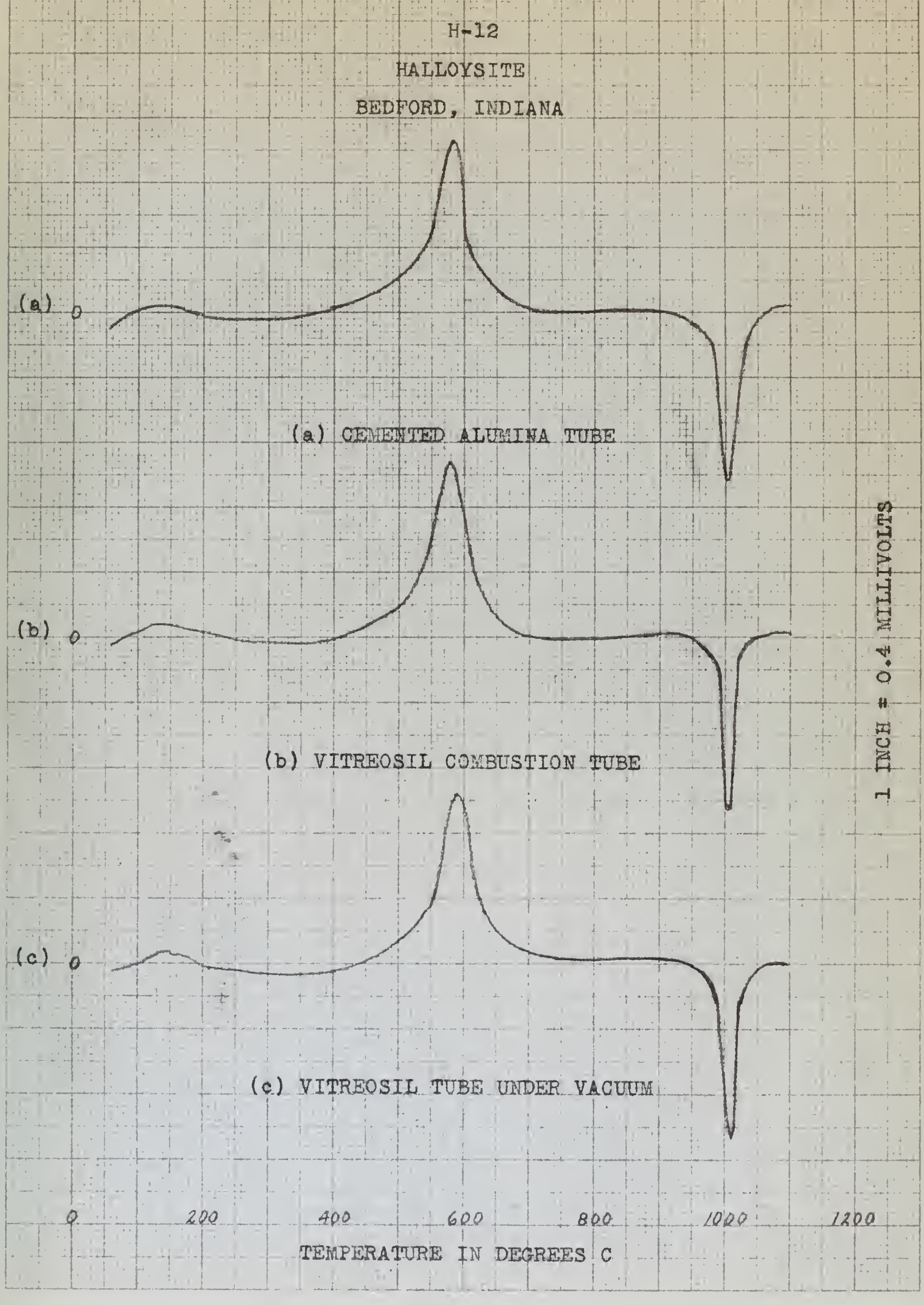

H-12
HALLOYSITE
BEDFORD, INDIANA
(a) 0
(a) CEMENTED ALUMINA TUBE
(b) 0
(b) VITREOSIL COMBUSTION TUBE
(c) 0
(c) VITREOSIL TUBE UNDER VACUUM
1 INCH = 0.4 MILLIVOLTS
0
200
400
600
800
1000
1200
TEMPERATURE IN DEGREES C

FIGURE 3

H-24

BENTONITE

OTAY, CALIFORNIA

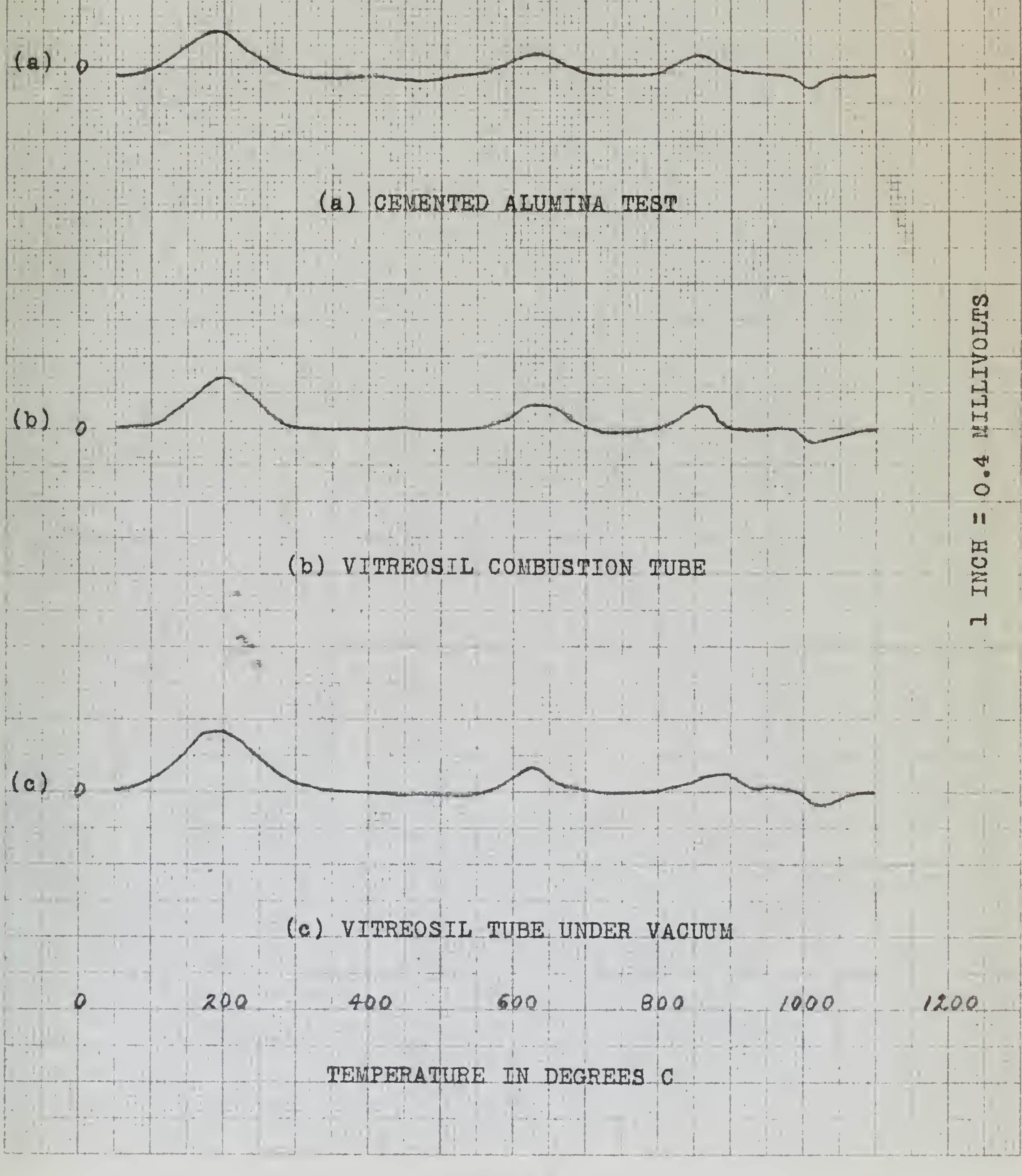


FIGURE 4

H-36
ILLITE
MORRIS, ILLINOIS

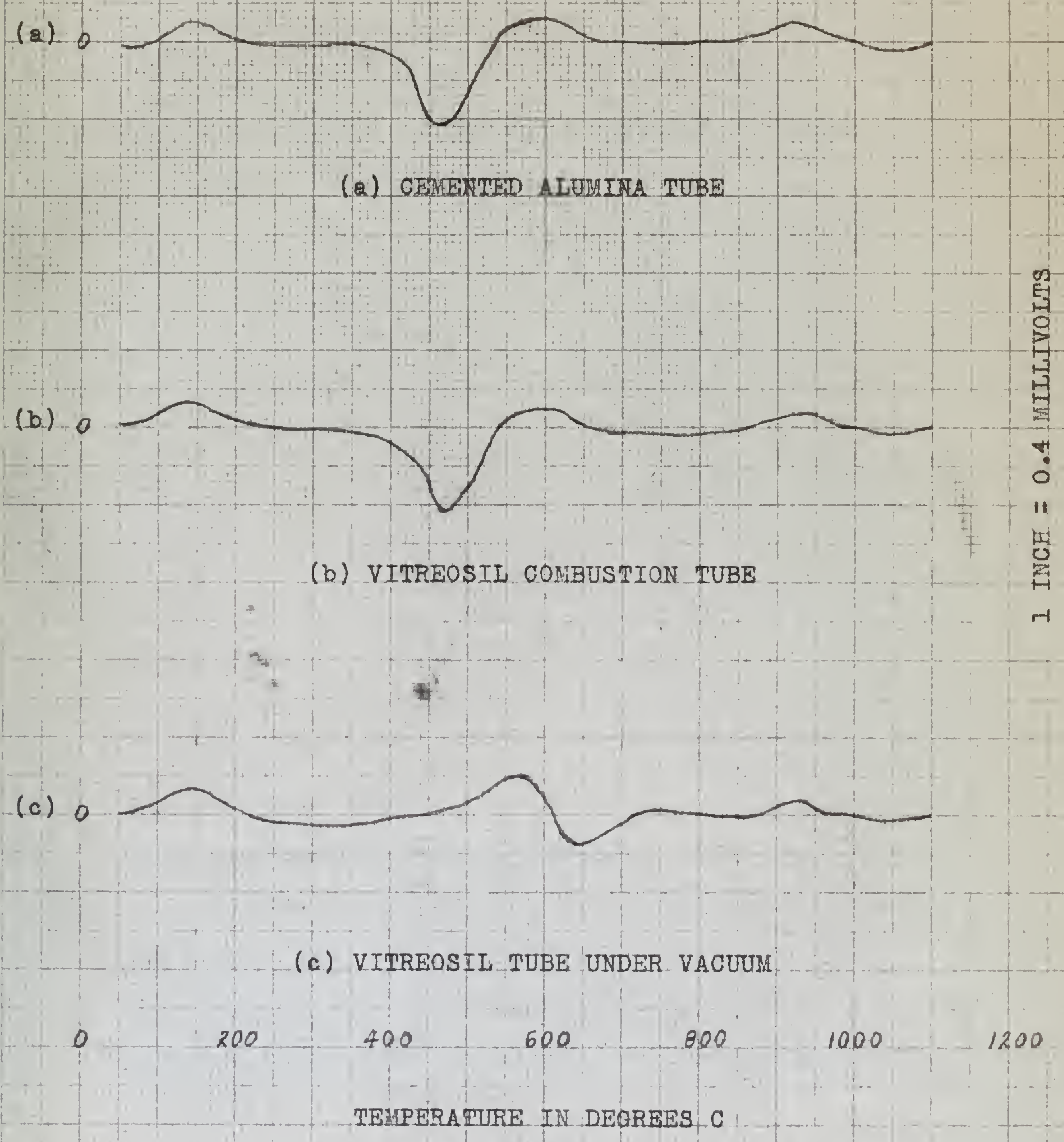


FIGURE 5

Record of Tests Conducted

I Tests run to verify accuracy of equipment and to obtain proficiency in use of equipment.

(a) Check heating rate of 1750-watt furnaces	6
(b) Differential thermocouple checks	9
(c) H-4 Kaolinite	4
(d) Cooling Curve	2

II Tests run to study the effects of a change in types of combustion tubes.

(a) Alumina in both sample and standard cells	4
(b) H-4 Kaolinite	2
(c) H-12 Halloysite	2
(d) H-24 Bentonite	2
(e) H-36 Illite	2

III Tests run to study the effects of the application of a vacuum to the sample.

(a) Alumina in both sample and standard cells	3
(b) H-4 Kaolinite	2
(c) H-24 Bentonite	2
(d) H-24 Bentonite	2
(e) H-36 Illite	2

Results of First Series of Tests

Because of the difficulty experienced by Merritt and White (17) with the 1750-watt heating elements in the furnaces, the first few test runs were made for the primary purpose of seeing how uniform a heating rate the

1750-watt furnaces would maintain. The results were highly satisfactory as well as informative. The large elements were able to maintain the rate set by the gear and chain-driven mechanism. The author had some trouble determining the initial setting on the compensating rheostat in order to maintain a uniform heating rate in the early stages of the analysis. This was overcome simply by a trial and error procedure until the correct setting was finally determined. This setting was finally determined to be between + 1.5 and + 2.0 on the scale of the rheostat. In conjunction with the heating tests, the calibration of the differential thermocouples was checked to make sure all tests would be made with an accurately recording differential thermocouple.

With regard to differential thermocouples, an incident that took place later in the tests is recorded here. In making a routine test, it was discovered that the differential thermocouple was not recording. This was confirmed by the use of a small soldering iron. The thermocouple had suddenly ceased to generate any e.m.f. even though a check with the thermocouple tester showed the circuit to be continuous. The thermocouple was removed from the sample holder and checked again. Although there was no visible evidence of any defect in the thermocouple, there was still no reaction to heating one of the two beads. The conclusion that the author

came to was that the bead had become oxidized to the point it was no longer sensitive. The circuit would still pass a directly applied voltage. This leads the author to wonder if possibly the life of all of the thermocouples is not a rather limited one, in which case, all of the thermocouples should be checked periodically by anyone making continued use of the equipment.

A series of four tests were run using H-4 Kaolinite. Two of these tests were run using "cell volumes" of both alumina and kaolinte, each material being in the grain size 200 mesh to pan. The results of these two tests were thermal curves which were similiar to the thermal curves obtained by Hoskins and Hudson (10) using a "cell volume" of kaolinite of this same grain size. However, the peaks obtained in the reactions were not as great as the peaks obtained by Hoskins and Hudson. They were on the order of one half the peak values obtained by the other investigators. The other two tests in this series were run using 0.7 grams of material in each cell. The thermal curves obtained checked very closely as to shape and magnitude of the reactions of the thermal curves obtained by Merritt and White (17) in their tests on similiar material of a like grain size.

At the conclusion of these tests, which were run for the sole purpose of familiarizing the author with

the techniques involved, it was felt by the author that he had an understanding of the mechanical problems involved in use of the equipment as assembled at Rensselaer Polytechnic Institute. The author also felt, that inasmuch as he had been able to reproduce the curves obtained by previous investigators, that future investigators would be able to reproduce any curves that might be obtained by the author.

Results of Second Series of Tests

The second series of tests were made necessary by the fact that, in order to apply a vacuum to the sample in the furnace, a combustion tube made of fused quartz had to be substituted for the cemented alumina combustion tube normally used in the furnaces. It was for this evaluation that the cemented alumina combustion tube in Furnace No. 2 was replaced by a combustion tube of fused quartz. Furnace No. 3 also had a fused quartz combustion tube installed, however, the one in Furnace No. 3 was 24 inches long compared to the 12 inch quartz combustion tube installed in Furnace No. 2.

There were twelve tests conducted for this evaluation of the effect of the change in combustion tubes. The composite thermal curves for H-4 Kaolinite, H-12 Halloysite, H-24 Bentonite, and H-36 Illite, obtained from these twelve tests are plotted as curves (a) and (b) on Figures 2, 3, 4, and 5.

Summarizing the results of these twelve tests led to the conclusion that, while the change in combustion tubes had little or no measurable effect on the location or magnitude of the reactions, it did affect favorably the displacement of the base line (the zero-millivolt line of the differential thermal curve).

The literature on the subject of differential thermal analysis has a great deal of information written on the subject of the shift of the base line. Harper and Kitterman (9) made a thorough investigation as to the nature of the cause of the displacement of the base line and concluded that the location of the displaced line is entirely a function of the materials (specifically the state of compaction, volume of materials, grain size, and other factors affecting the thermal conductivity of the materials). Harper and Kitterman also concluded that a reheat thermal curve would provide a "true base line" for the measurement of the magnitude of the reactions.

Grim (5) says that in order to maintain the horizontal position of the base line of the differential temperature curve, it is necessary to maintain thermocouple beads of constant size and to keep the beads in the centers of the sample and reference material. Grim also makes reference to the "coefficient of thermal diffusivity" of the material which he defines as the

rate at which a point in a hot body will cool under definite surface conditions. He considers that the diffusivity of the specimen may change as it is heated because of the formation of new phases at high tempertures or because of shrinkage of the sample. The effect of a gradual change would be to produce a sloping base line, and a sudden change would produce an offset in the base line.

The author agrees that the primary cause of shifts in the base line can be attributed to the changes which take place in the thermal conductivity of the sample, however, the results of the tests conducted by the author, which show that a change in type of combustion tubes has an effect on the base line, disprove the statement that a shift in base line is entirely a function of the materials being tested. It is also very difficult for the author to accept the theory of Harper and Kitterman that the reheat differential temperature curve is the "true base line". After an "active" material has been subjected to temperatures up to 1000°C, it is inconceivable to the author that it will have the same thermal conductivity at different temperatures in a reheat curve as it had at the same temperatures in its initial heating curve. The change caused by the different combustion tubes was toward a more uniform base line, however, the change was quite small, and therefore it

is believed that the curves obtained from the quartz combustion tubes will be able to be compared to curves obtained from cemented alumina combustion tubes without fear of introducing a new variable into a system already well supplied with variable factors.

Results of Third Series of Tests

The third series of tests were those where the actual work done in evaluating the effects of a vacuum applied to differential thermal analysis was accomplished. The initial tests were run on kaolinite because of the familiar, well-defined thermal curve that could be expected. Then later on, tests were run in turn on a halloysite, a bentonite, and an illite. The composite thermal curves obtained from these tests are plotted as curve (c) on Figures 2, 3, 4, and 5, for each of the minerals.

Three of the minerals tested were relatively pure clay minerals and their reactions were affected only slightly by the application of the vacuum during the period of the analysis. The locations of the reactions were not affected, but the inflection points of the curves were somewhat sharpened.

In the case of the illite, however, there was a very noticeable reaction. Whereas the normal thermal curve for the illite showed a sharp exothermic reaction at approximately 460°C, the vacuum thermal curve showed

a conventional second endothermic reaction at approximately 570°C , and this reaction was followed by a much smaller exothermic reaction at approximately 640°C. The illite which was used is known to contain a fairly large amount of siderite and certain organic material. It is the author's belief that the vacuum prevented the rapid oxidation of the organic material which had caused the large exothermic reaction at 460°C, and that the exothermic peak which did occur can be attributed to the siderite present in the sample.

Curves of this particular illite are shown by Kerr, Kulp, and Hamilton (13) after leaching with dilute HCl. These curves agree very closely with those of the author and strengthen his belief that the vacuum tends to reduce the effect of any impurities, and in the case of organic matter, eliminates the confusing aspects of the curve altogether.

This is a significant fact, as the presence of organic matter in the fine fraction of soil and clay materials has long made difficult the identification of the minerals present in the material. Chemical treatment is the usual solution to this problem and attempts are made to oxidize the material through the use of oxidizing agents. However, in the case of clays with a high base exchange capacity, an exchange can take place. Where the concentration of the oxidizing

agent is such that the vigorous action needed is obtained, this action may disrupt the clay mineral lattice to such an extent that any subsequent results obtained are possibly quite different from what is truly representative of the field conditions.

It is the author's belief that the normal oxidation of the organic material is prevented, and, instead of a rapid oxidation, which would produce an exothermic reaction, the organic material either vaporizes directly or breaks up in a pyrolysis effect. The process of pyrolysis is a breaking up of large unsaturated molecules into smaller molecules which then vaporize. Both the vaporization and pyrolysis occur over a wide temperature range and because the heat of vaporization is about 1/6 to 1/10 that of water, there is not sufficient change at any time to affect the magnitude of the reactions.

The author regrets that there was not sufficient time available for more work on the subject of the organic material in clays, because it is believed that the use of vacuum technique will prove a valuable adjunct to the established process of differential thermal analysis.

CONCLUSIONS AND RECOMMENDATIONS

In consideration of the tests run and the literature studied, the following conclusions are drawn:

1. The nature of the heat control mechanism is such that great care must be taken in starting the mechanical timer of the Brown Potentiometer. If the temperature begins to lag the timer, it will overcorrect itself and this will result in a "hunting effect" which will cause the heating rate to be very erratic, and, once started, in a particular run, it is almost impossible to eliminate the variations taking place in the actual heating rate.
2. The use of a quartz combustion tube does affect the thermal curve, but it is a favorable effect in that it tends to lessen the displacement of the base line from the zero millivolt line. This slight effect can be evaluated so as to make thermal curves comparable with other thermal curves for quantitative analysis.
3. Because of the nature of the reactions taking place in a pure clay, that is either a dehydration or a decomposition, both of which are purely a function of the temperature and the nature of the mineral, the presence or absence of a normal atmosphere has no effect on these reactions. However, in the case

of a sample which contains sizeable amounts of organic material, the use of a vacuum technique may very well prove to be a valuable tool in the application of the process of differential thermal analysis to such a sample. Vacuum technique may very well make unnecessary all of the applications of oxidizing agents to soil samples suspected of high organic material content, and thereby eliminate the danger of an exchange process occurring which may mask or change the true nature of the soil. It is the author's belief that the vacuum technique has a definite place in the Soils Laboratory and that it will prove a valuable aid in the difficult job of identifying soil samples containing substantial amounts of "clay-size" particles, a portion of which are of organic nature.

In the interest of continuing the extension of the application of differential thermal analysis to soil identification, the following recommendation is offered:

It is recommended that the technique of vacuum thermal analysis be studied further with the emphasis being placed on its effect on organic materials in soils. It is also suggested that the application of atmospheres of an inert gas such as nitrogen or orgon might be studied. These gases should theoretically

have the same effect as the vacuum, in that the oxygen necessary for rapid oxidation of the organic material is eliminated.

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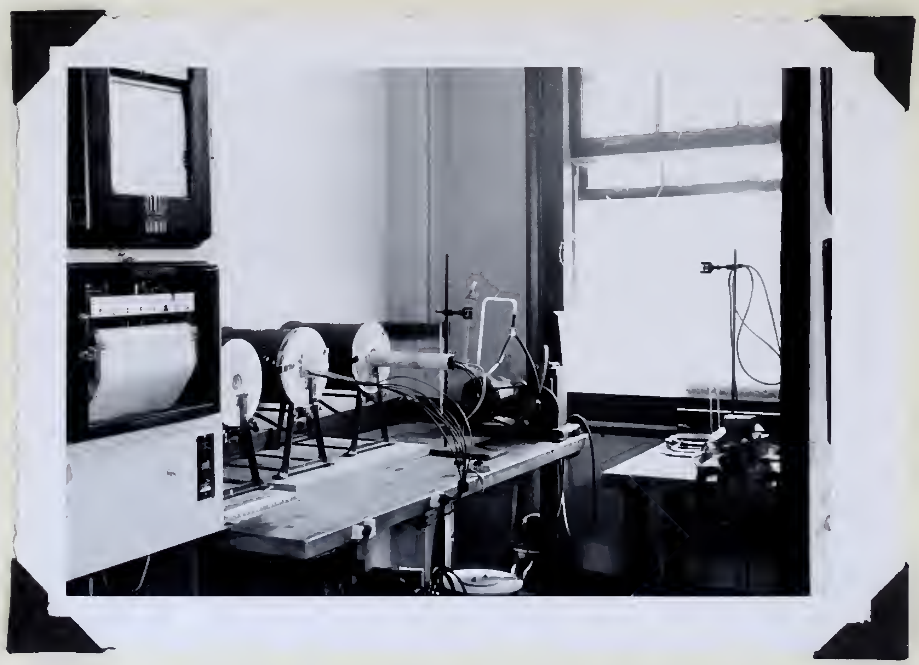
APPENDIX A

1. Laboratory Work Area and Sample Preparation Table
2. General Views of Equipment
3. Recording Equipment
4. Vitreosil Combustion Tube and Special Sample Holder
5. Furnaces and Vacuum Pump

Laboratory Work Area

Sample Preparation Table

General View of Equipment



General View of Equipment

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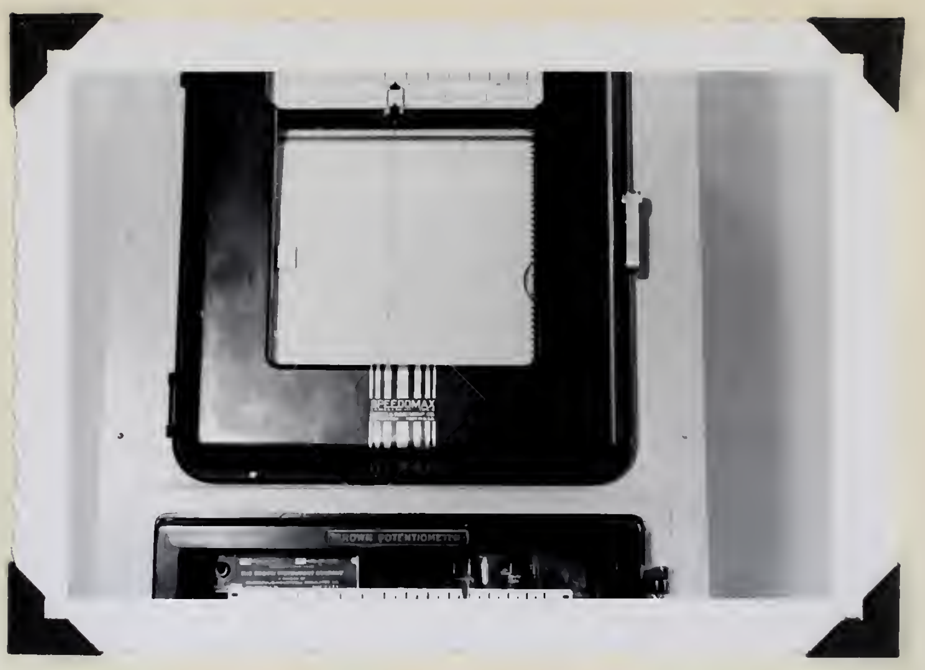
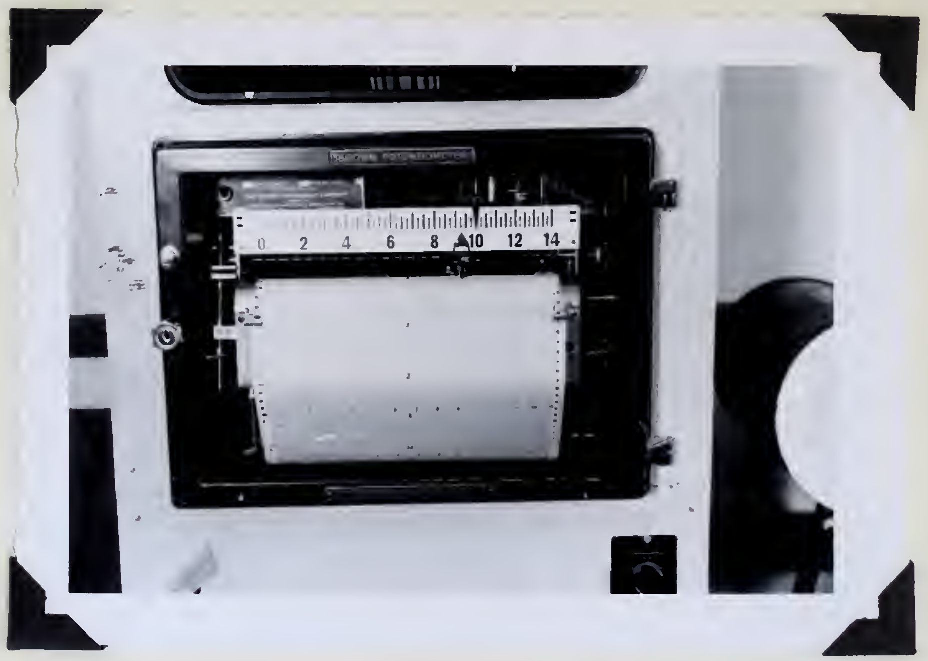


Speedomax, Type G, Model S 60000 Series



Brown Recording Potentiometer

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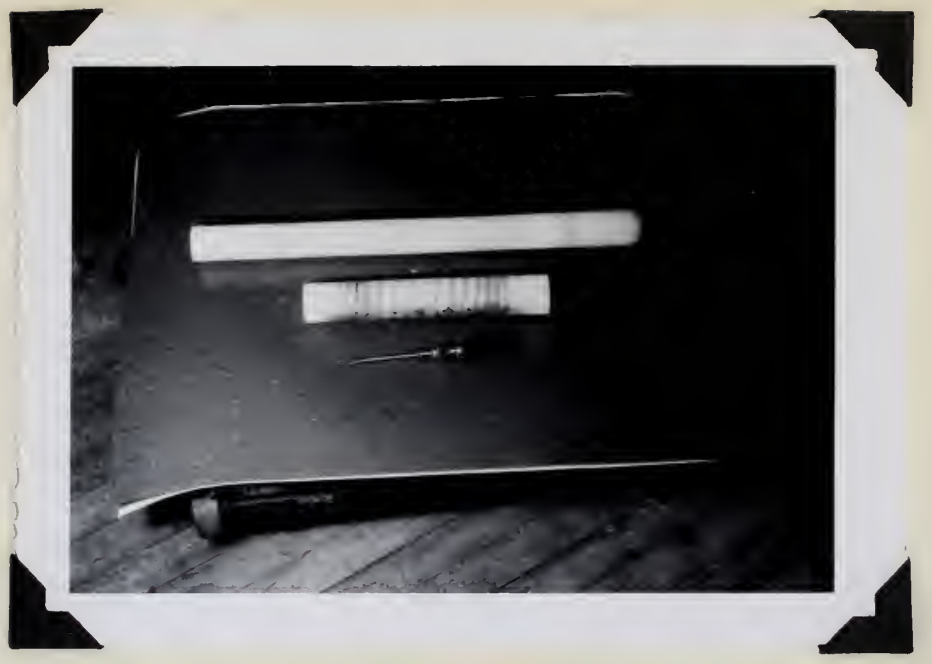
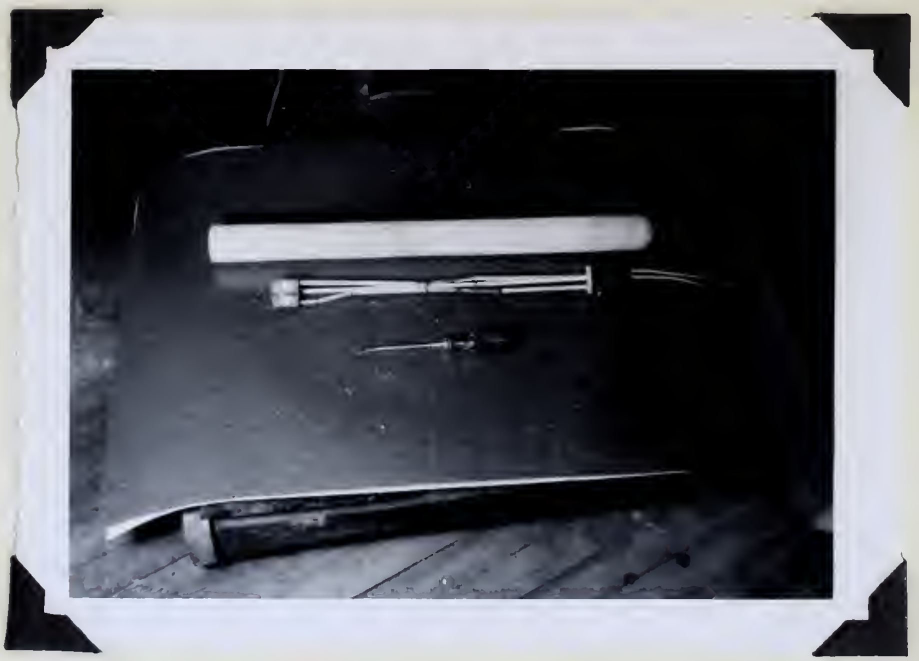


Vitreosil Combustion Tube and

Cemented Alumina Combustion Tube



Vitreosil Combustion Tube

Special Sample Holder

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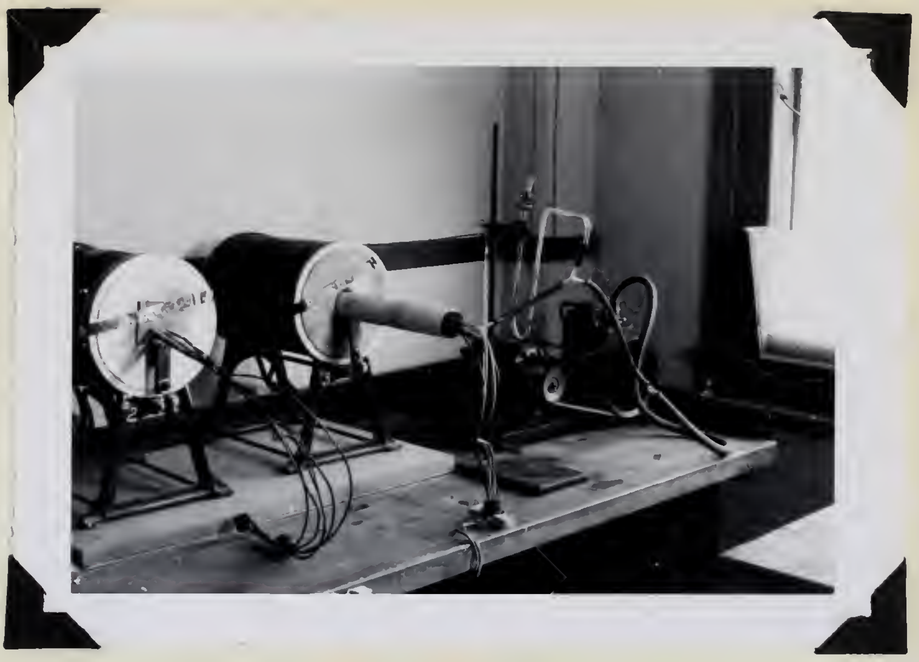
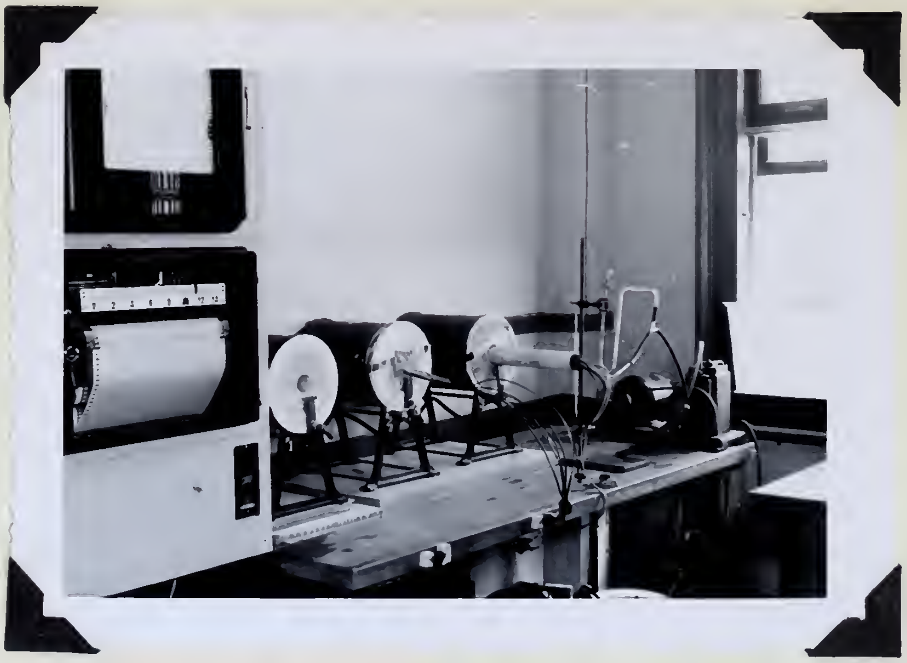


Furnace #3 with Vacuum Pump



Furnaces and Vacuum Pump

APPENDIX B

Samples of Curves Obtained

TEST No. 11

H.4 KAOLINITE
200 - PAN (GRAIN SIZE)
8 APRIL 1954
1750 WATT FURNACE No. 3
ATMOSPHERIC PRESSURE

TEST # 23

H 4 KAOLINITE
200-PAN (GRAIN SIZE)
3 MAY 1954
1750 WATT FURNACE No 3
UNDER VACUUM

TEST No 18

DIFFERENTIAL THERMOCOUPLE CHECK
ALUMINA IN BOTH CELLS
SAMPLE HOLDER (SPECIAL)
FURNACE No 3
27 APRIL 1954

Thesis
28822
M557 Miller
A study of the effect of vacuum and pressure applied to differential thermal analysis.

Thesis
28822
M557 Miller
A study of the effect of vacuum and pressure applied to differential thermal analysis

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